

Supporting Information for:

PAH Concentrations in Lake Sediments Decline Following 2006 Ban on Coal-Tar-Based Pavement Sealants in Austin, Texas

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Contents

Figures S-1, S-2, and S-3

Estimation of PAH non-detections

Age Dating of 2012 Cores

Effects of the 2007 Flood

References for PAH source profiles in Table S-5.

Tables, provided separately in Microsoft Excel® format

Table S-1. Radionuclide activities for samples from Lady Bird Lake cores.

Table S-2. Concentrations of PAHs, selected other organic compounds, and organic carbon in Lady Bird Lake cores and bottom sediment sampled in 2012 and 2014.

Table S-3. Concentrations of PAHs and selected other organic compounds in Lady Bird Lake (formerly Town Lake) samples collected in 1998 to 2001.

Table S-4. Concentrations of the 16 EPA Priority Pollutant PAHs with non-detected values replaced by estimated values, as described herein.

Table S-5. Proportional concentrations of 12 PAHs in 22 potential PAH sources. Source material references are included herein.

Table S-6. Chi square (X^2) test statistics between PAH profiles for 22 potential sources (presented in Table S-5) and PAH profiles in sediment samples from Lady Bird Lake. Source material references are included herein.

Table S-7. Summary of results of Contaminant Mass Balance modeling of PAH sources to Lady Bird Lake sediments.

Figures

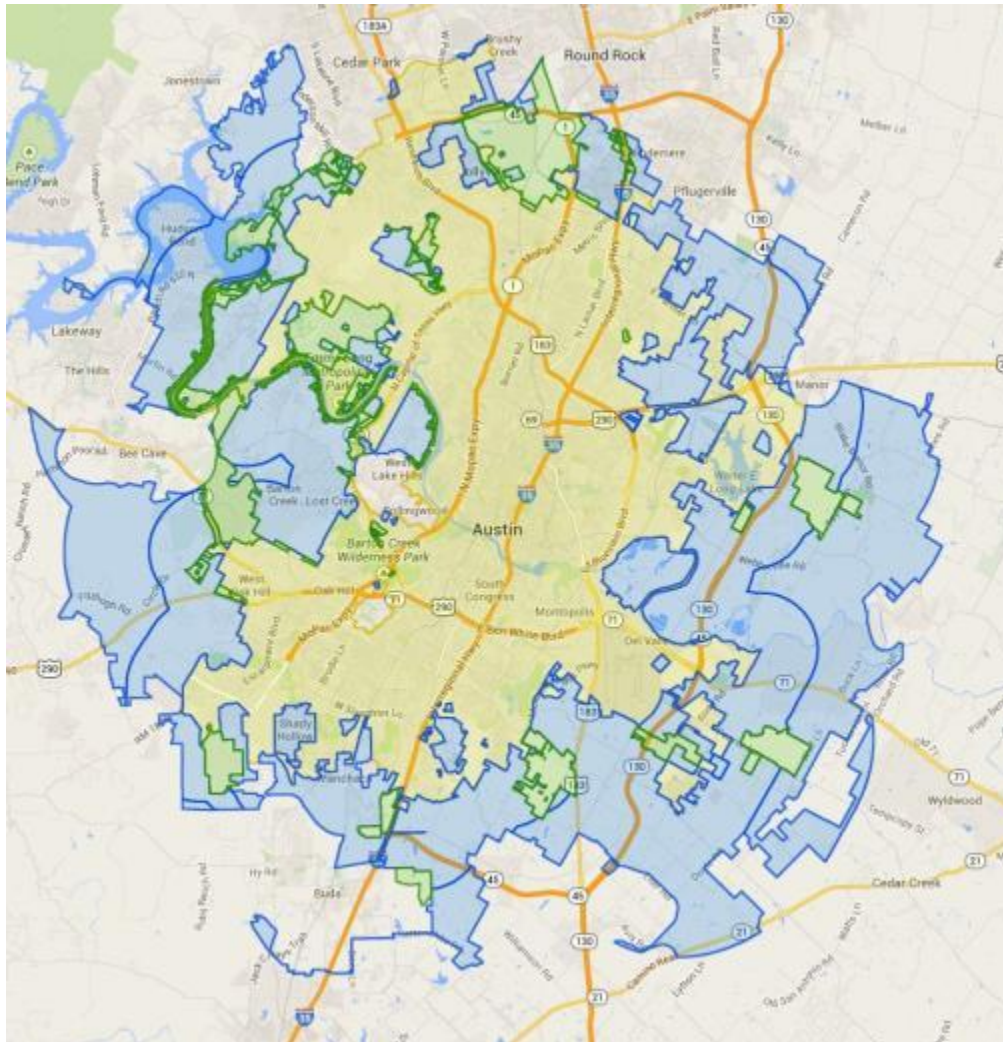


Figure S-1. City of Austin, TX (light yellow shade), and its Extra Territorial Jurisdiction (ETJ, blue and green shades). Accessed May 21, 2014 at:

<https://maps.google.com/gallery/details?id=z2BTfOh7kE5U.kArgfpJfEqYQ&hl=en-US>.

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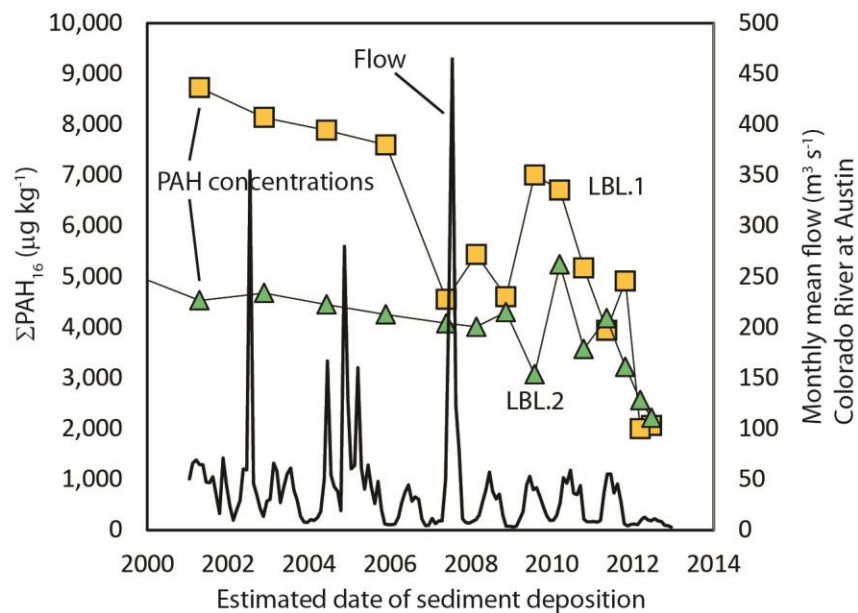


Figure S-2. Trends in the sum of the concentrations of the 16 U.S. Environmental Protection Agency Priority Pollutant PAHs (ΣPAH_{16}) in sediment cores LBL.1 and LBL.2 collected in 2012 from Lady Bird Lake and monthly mean streamflow in the Colorado River at Austin (USGS streamgage 08158000).

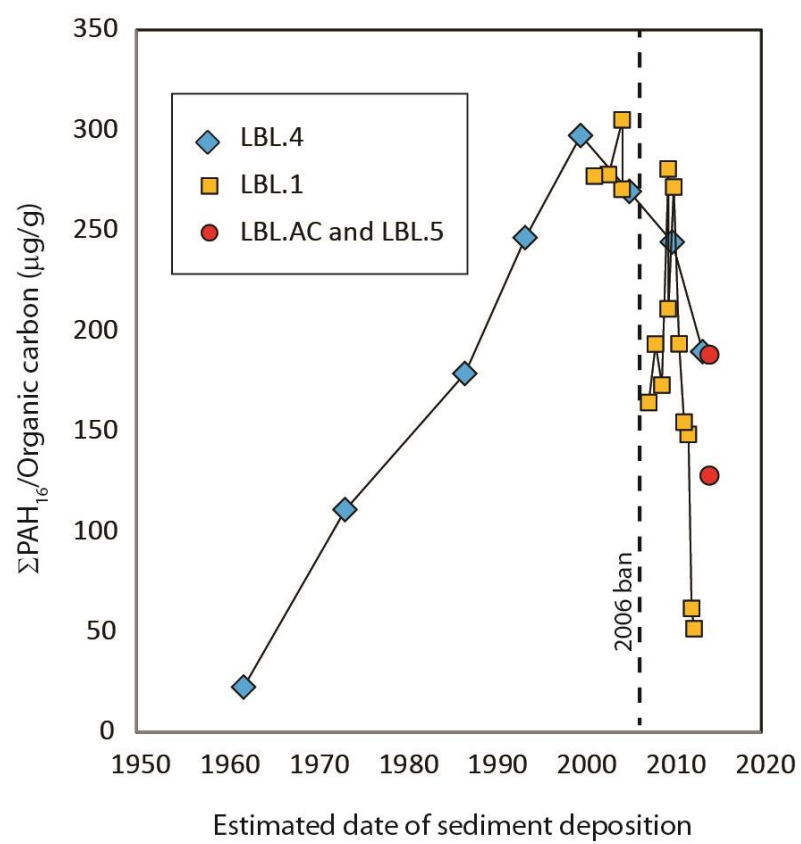


Figure S-3. Concentrations of ΣPAH_{16} normalized to organic carbon in sediment samples collected from the lower lake sites in 2012 and 2014.

Estimation of PAH non-detections

Non-detections for the 2012 cores were infrequent for most parent PAHs; 11 of the 16 EPA Priority Pollutant PAHs were detected in all 16 samples from core LBL.1 and 10 of 16 were detected in all 20 samples from core LBL.2, and 12 of 16 EPA Priority Pollutant PAHs were detected in all samples. However, 2 of the 16 EPA Priority Pollutant PAHs—fluorene (Flo) and dibenzo[*a,h*]anthracene (DaA)—were reported as non-detections for all samples from cores LBL.1 and LBL.2. DaA and indenopyrene (IP) are known to co-elute, which can be problematic if IP is present in appreciably higher concentrations than DaA; for those TWN.1 samples in which both PAHs were detected (1998 core) the mean ratio of IP:DaA was 5.2:1. Any potential DaA detections in the LBL.1 and LBL.2 samples likely were masked by the larger co-elution of IP. Matrix interferences are uncommon for Flo; however, most samples from LBL.1 and LBL.2 cores showed the quantitation ion out of proportion to the Flo concentration and interference on one of the two qualifier ions. Thus, for these samples, two of three ions that are used to quantify and verify the identification of the compound (Flo) did not meet qualification criteria, which resulted in raised reporting levels and non-detections in all of the LBL.1 and LBL.2 samples (Teresa Burbank, U.S. Geological Survey, written communication, May 8, 2013).

Non-detections for the 2014 cores also were infrequent for parent PAHs; the 16 EPA Priority Pollutant PAHs were detected in all 15 samples and there were 10 non-detections among the 240 possible values. The analytical issues with Flo and DaA in the 2012 core analyses were not evident in the 2014 core analyses, with Flo detected in all 15 samples and DaA detected in 14 of 15 samples.

PAHs are a group of related compounds that, for a given environmental setting, tend to be strongly correlated to each other in relatively consistent patterns, as indicated by the

widespread use of PAH isomer ratios and chemical profiles in source analysis¹⁻⁵. The concentrations of those PAHs detected therefore can provide useful information on the probable concentrations of some non-detections, providing an alternative to other missing-value estimation methods⁶. Non-detections were estimated by (a) determining correlations between the 16 EPA Priority Pollutant PAHs reported for samples in the TWN.1 core in which all 16 PAHs were detected, (b) identifying the PAH with the strongest correlation to each PAH with a non-detection in the LBL.1, LBL.2, LBL.4, and LBL.5 cores, (c) computing the ratio of those two PAHs (where both were detected) in the TWN.1 core, (d) using this ratio to estimate the likely concentration of the non-detected PAH, and (e) comparing that estimation to the reporting level in the sample and using whichever value was lower. Pearson's r values for the PAH pairs used for estimation ranged from 0.78 to 0.99.

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Age Dating of 2012 Cores

Deposition dates were assigned to the sediment intervals in cores LBL.1 and LBL.2, both of which were collected with a box corer, by estimating the sedimentation rate on the basis of the dates assigned to core LBL.3, a gravity core, and applying an assumed amount of core shortening in LBL.3. The box cores could not be dated directly because they are too short to have penetrated to the 1963-64 ^{137}Cs peak or the pre-reservoir sediment interface. Free-fall gravity cores are subject to core shortening, that is, the thinning of soft sediments during sampling by wall friction and back pressure within small-diameter free-fall corers ¹. Shortening does not affect cores collected by larger diameter, slow-entry corers such as box corers. In side-by-side core collection, we have found core shortening of about 40% for a core collected with a 6.3-cm diameter free-fall gravity corer relative to cores collected with piston and 14x14-cm box corers ². We therefore assumed 40% core shortening in LBL.3 relative to LBL.1 and LBL.2; after applying the resulting correction to the mass accumulation rate (MAR) calculated for LBL.3, we used the adjusted MAR to estimate deposition dates for LBL.1 and LBL.2. The resulting MAR ($0.62 \text{ g cm}^{-2} \text{ y}^{-1}$) indicated that the deepest sample analyzed for PAHs in LBL.1 (17–18 cm) was deposited in about 2001 and in LBL.2 was deposited in about 1996 (23–24 cm). However, as described below in Effects of the 2007 Flood, sediment deposition in both cores appears to have been affected by a large flood on the Colorado River in Austin in July 2007— during July 2007, U.S. Geological Survey streamgage 08158000 Colorado River at Austin, TX, recorded the largest flood in the past 20 years on the basis of monthly mean discharges ³. In core LBL.1, flood-related sediment appears to occupy about a 4-cm interval, from 7 to 11 cm depth, in the core. In LBL.2, sediment from about 6 cm depth to the bottom of the core (25 cm depth) appears to have been disturbed by flooding, and this core therefore is considered less reliable than core LBL.1 for indicating pre-2007 PAH concentrations.

Extrapolation of dates from one core to a nearby core has large uncertainty because of spatial variability in sedimentation rates² and, in this case, the estimation of a core-shortening correction factor. Uncertainty in age dating, however, decreases toward the top of the core⁴⁻⁵, and the primary objective of this study was to evaluate recent, post-2006, trends in PAHs. Thus, although deposition dates of samples deeper in the cores are less certain, we are confident that the top of cores LBL.1 and LBL.2 corresponds to August 2012, 6.5 years after the ban on CT sealants. We also are confident in the age dating of core LBL.4 (collected in 2014), concentrations and trends in PAHs previously reported for the 1998 TWN.1 core^{2,6}, and PAH concentrations in the 2000 and 2001 bottom sediment samples TWN.2, TWN.AC, TWN.BC, TWN.CC, AND TWN.DC. If we were to assume the dates for pre-2008 portions of core LBL.2 were correct, ΣPAH_{16} concentrations in LBL.2 decreased from a mean of $4,580 \mu\text{g kg}^{-1}$ in pre-2006 samples to $2,390 \mu\text{g kg}^{-1}$ in the two most recently deposited samples, a decrease of about 48%. A significant downward trend in ΣPAH_{16} also is indicated by the six most recent samples from LBL.2 ($r = -0.92$, $p\text{-value}=0.009$).

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Effects of the 2007 Flood

The decrease in $\sum\text{PAH}_{16}$ in core LBL.1 in sediments dated as deposited in 2009 or later is preceded by a pronounced decrease or “dip” in concentrations at depths from 7 to 11 cm in the core (Figure S-2). On the basis of deposition date estimates for the core, this dip coincides with a large flood in 2007 on the Colorado River. Sediment transported from the mostly undeveloped, 100,000 km² watershed of the Colorado River normally is trapped in reservoirs upstream from Lady Bird Lake, but “torrential rains” in the upland region to the west of Austin prompted floodgate releases from the upstream reservoirs in 2007¹. During this major flood, some of the sediment from upstream likely was deposited in Lady Bird Lake, diluting concentrations of runoff contaminants, including PAHs, from local urban sources. It is likely that the MAR was substantially higher during the flood, and that the dip in $\sum\text{PAH}_{16}$ therefore represents a relatively short depositional period – weeks to months in 2007 – rather than the ~3 y estimated assuming a constant MAR. Deposition of flood sediments might also explain why there is an apparent lag between the 2006 sealcoat ban and the rapid decrease in $\sum\text{PAH}_{16}$ beginning at the estimated core date of about 2009 (Figure S-2). The similarity in PAH concentration in the deepest samples in core LBL.1 (mean of 8,090 $\mu\text{g kg}^{-1}$) and in the bottom-sediment samples collected in 2000 and 2001 in the lower lake (TWN.AC and TWN.2) and samples in cores TWN.1 and LBL.4 with deposition dates during 1998–2005 (mean of 7,890 $\mu\text{g kg}^{-1}$; see manuscript Figures 2 and 3) indicates that the deeper parts of core LBL.1 are representative of the early 2000s time period.

Recent (2007–12) PAH trends in cores LBL.1 and LBL.2 are similar, but concentrations in samples dated as deposited before about 2007 diverge (Figure S-2). The difference in $\sum\text{PAH}_{16}$ concentrations and trends in the deeper sediment intervals might be related to the 2007 flood.

PAH concentrations in LBL.2 sediments dated as deposited in about 2008 or before (core depths

from 6 to 24 cm) are constant within expected analytical uncertainty ($4,450 \pm 315 \mu\text{g kg}^{-1}$) and are similar to concentrations in core LBL.1 during the flood-related dip in concentrations. The differences in PAH concentrations between cores in deeper intervals are not explained by differences in organic carbon concentrations in the cores, which are similar (Supporting Information, Table S-1). The relatively low concentrations and lack of a trend below 6-cm depth in core LBL.2 indicates that there might have been rapid sedimentation at the LBL.2 site during the 2007 flood. The two cores were collected within ~50 m of one another, but it is not uncommon for cores from nearby locations in reservoirs to have different sedimentation patterns and rates². Because of the uncertainty regarding the representativeness of the lower part of core LBL.2, use of data from this core was limited to the top two intervals, which were deposited in 2012. We note, however, that comparison of those two intervals to the mean $\sum\text{PAH}_{16}$ concentration in the 6-24 cm intervals in this core indicates a 45% decrease in PAH levels.

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